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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods
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DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Other draft amendments

Listing and classification
Lithium Batteries

Transmitted by the Expert from the United States

Introduction

1. Rapid advancement is being experienced in the development of new lithium battery technologies. For a variety of reasons, lithium batteries employing newer technologies do not present the same level of hazard in transport that are presented by the older lithium battery technologies, particularly from the point of view of the types of dangerous goods that may be contained in such batteries and the potential for release of these substances from the battery. However, such batteries continue to pose a hazard from the point of view of the stored energy contained in a charged battery, as well as from the "water-reactive" hazard associated with metallic or other forms of lithium that may be present. The size of lithium batteries has also increased dramatically in light of these developments, with very large batteries now being produced for various applications, including for purposes of electric vehicle propulsion. As these new types of lithium batteries are brought into large-scale production for commercial purposes, the need to consider appropriate international requirements to ensure both the safe, and efficient, transport of such batteries has become urgent.

2. The current lithium battery transport provisions in the Recommendations, and the associated tests in Section 38.3 of the UN Manual of Tests and Criteria, pose serious practical obstacles to the transport of these newer technology, larger sized lithium batteries and cells for several reasons, including the following:

(a) The Recommendations currently make no provision for the transport of "large" (i.e., with lithium contents exceeding 12 g per cell or 500 g per battery) lithium cells and batteries;

(b) Under the current test regime, the testing costs for "large" batteries and cells would be excessive in relation to the lower production volume and higher unit costs of such batteries and cells; and

(c) The current tests do not take appropriate account of certain characteristics of the newer technology, larger cells and batteries, such as the voltages exhibited, their resistance to capacity reduction through cycling and the cycle-time necessary to achieve currently specified testing conditions.

Accordingly, to take account of progress in science and technology related to lithium batteries, as well as of the increased sizes and unit costs (and the correspondingly lower rate of production) of such batteries, this document proposes various amendments to the current provisions governing the transport of lithium batteries.

Discussion

3. The two main new lithium battery technologies may generally be described as "lithium polymer" batteries, and "lithium ion" batteries -each of which, as in the case of most types of batteries, consists of one or more cells. Each of these two main types of new lithium battery technologies is described in general terms below:

(a) *Lithium polymer batteries and cells.* Lithium polymer batteries and cells contain no liquid or gaseous components. Although designs vary, lithium polymer cells typically consist of a polymeric lithium ionic conducting membrane with two lithium reversible electrodes. The polymeric ionic membrane acts both as an electrolyte, and as a separator between the electrodes. The polymer membrane is typically a high molecular weight polymer (e.g., polyethylene oxide) with a dissolved lithium salt. The negative electrode is typically a lithium metal foil. The positive electrode consists of a material based on a reversible intercalation compound which is blended with the high molecular weight polymer/lithium salt electrolyte and carbon so as to form a plastic composite that is backed by a metal foil current collector.

The most significant "chemical" hazard posed by lithium polymer cells and batteries is that associated with the potential reactivity of water with the lithium metal foil.

(b) *Lithium ion batteries and cells*. Lithium ion batteries and cells contain no gaseous components, no free liquid components (generally), and in almost all cases no metallic lithium. If metallic lithium is present, it would be only after numerous cycles and/or after extreme abuse, and only in minute quantities. A typical lithium ion system consists of an inorganic lithium intercalating compound as the positive electrode, a lithium salt in an organic liquid or a lithium ion conducting polymeric membrane as the electrolyte, and a lithium-intercalating carbon negative electrode. Lithium ion conducting solid polymer electrolyte membranes can act both as the electrolyte, and as the separator between the electrodes. Organic liquids used in electrolytes are typically composed predominately of relatively high flashpoint cyclic carbonates, such as ethylene carbonate and propylene carbonate. The name *lithium ion* is used to distinguish such systems, which normally do not contain metallic lithium, from systems with metallic lithium negative electrodes.

The most significant "chemical" hazard posed by lithium ion cells and batteries is that associated with the lithiated carbon electrode of a charged cell or battery. While significantly less reactive with water than metallic lithium, the lithiated carbon electrode matrix would, like metallic lithium, meet the criteria for classification in Division 4.3. However, new, uncycled and uncharged lithium ion cells and batteries may contain no components exhibiting a hazard of reactivity with water. In addition, although some electrolytes may meet the criteria for Class 3, the quantity of electrolyte, and the manner in which it is retained within the cell or battery, is such that the electrolyte will normally not flow from a ruptured or cracked casing.

For purposes of transport, however, the expert from the United States believes that cells and batteries employing these newer technologies may nevertheless generally be considered to fall within the current "lithium battery" entry in the Dangerous Goods List, and that this should be clarified by an appropriate amendment to Special Provision 230.

4. Some of the most serious practical problems with the current provisions for lithium batteries arise from the limitations in Special Provision 230 on the quantity of lithium or lithium alloy that may be contained in any cell or battery (i.e., 12 g and 500 g, respectively). These limitations are far too low to accommodate current "large" lithium polymer batteries and cells, and, since lithium metal is not present in lithium ion batteries, are not clearly relevant in relation to lithium ion batteries. While originally intended to provide a limitation on the maximum stored energy that may be present in a lithium battery, such limitations are no longer considered necessary or appropriate in light of the test methods currently contained in the Manual of Tests and Criteria -which thoroughly assess the risks posed by a battery or cell in terms of stored energy, and ensure that such risks do not exceed an appropriate level. Therefore, this document will propose that the cell and battery lithium or lithium alloy quantity limitations be removed from Special Provision 230, and be used only in the Manual of Tests and Criteria for purposes of determining the number and condition of cells and batteries to be tested. A note to this effect would be added to Special Provision 230.

5. In all current forms of lithium batteries, lithium is the only chemically active species in the negative electrodes. It can be present in a variety of forms: pure lithium metal, combined with chemically inert metals as metal alloys, or intercalated into chemically inert carbon or graphite hosts. Therefore, the energy content of a lithium cell or battery is controlled by the quantity (mass) of lithium present in the anodes. Actually, when the lithium is bound in a metal alloy, carbon, or graphite host, its chemical activity (and associated safety hazard) is suppressed for an equivalent quantity of lithium present. Therefore, in this proposal, to the extent that the 12 g/cell and 500 g/battery mass limits would continue to appear in the Test Manual, the limitations would apply to the "lithium content" of the negative electrodes and not to the mass of "lithium or lithium alloy" in cells or batteries (as it appears in the current Recommendations).

6. Paragraph (f) of Special Provision 230 currently requires cells or series of cells connected in parallel to be equipped with diodes "to prevent" reverse current flow. The expert from the United States believes that other appropriate means (such as fuses) may be employed to prevent dangerous reverse current flow. Moreover, reverse current flow is essential to allow the recharging of secondary cells and batteries. Therefore, it is proposed that this provision be revised to remove the specific reference to use of "diodes to prevent reverse current flow", and replace it with reference to use of "effective means to prevent dangerous reverse current flow". The term "effective means" is currently employed in paragraph (e) in relation to external short circuit prevention.

7. The Recommendations currently provide that, except for transport by air, both "wet batteries" installed in vehicles and sodium batteries installed in vehicles are not subject to the Recommendations. In the interest of consistency, this document proposes that a similar exception be incorporated for lithium batteries installed in vehicles.

8. Of the six "series T" tests prescribed in the Manual of Tests and Criteria, all tests are considered relevant to large, lithium polymer or lithium ion cells and batteries in terms of assessing the potential risks posed by those cells or batteries in transport. However, while such tests are considered generally relevant to "large" lithium polymer and lithium ion cells and batteries, for the reasons outlined previously the current provisions in the Manual of Tests and Criteria regarding the number of cells and batteries required to be tested are in certain respects considered inappropriate for large cells and batteries. For these reasons, this document proposes that the Manual of Tests and Criteria be amended to provide for the testing of an appropriate number of "large" cells and batteries -each under the appropriate conditions of cycling and charge -consistent with the need to ensure the necessary level of safety in the transport. In this connection, it is emphasized that since all large lithium cells and batteries are rechargeable (owing to their high cost of production), it has not been found necessary to address "primary" cells and batteries in the proposed amendments to the Test Manual.

9. Specifically, it is proposed herein that cells and batteries employing negative electrodes with lithium contents not exceeding 12 g and 500 g, respectively, would be required to be tested in number and under conditions as provided in the current Manual of Tests and Criteria. Larger cells and batteries (i.e., those not currently addressed in the Recommendations), would be subject to all the "Tests" prescribed in the Test Manual, except that in certain cases the number and charge condition of cells and batteries to be tested would be reduced or altered, in accordance with the following:

(a) Test T.1 and Test T.2. Except where cells are to be transported individually, tests would be required to be performed only on batteries because this is considered to be a more "extreme" level of testing, and because the performance of individual cells (within batteries) under similar tests is assessed in Test T.3. The number of batteries to be tested (4), is the same as that currently required by the Test Manual for "small" lithium batteries.

(b) Test T.3. Tests would be performed only on cells, because the voltage constraints imposed by the "Charge test" procedure (see 38.3.4.3.3.3) precludes the test from being performed at the battery level. To stay within the prescribed "12 volts/V" constraint, the tests would be performed on series-connected strings composed of 3 or 4 cells, each having a nominal voltage in the range of 3 to 4 volts. Thus, for example, two 4-volt, or three 3-volt fully-charged cells would be connected in the normal manner, and the third 4-volt or fourth 3-volt fully-charged test cell would be connected with the reverse polarity and in series with the specified load. This would force the test cell into an overcharged state. The number of cells to be tested (10), is the same as that currently required by the test manual for "small" lithium cells.

(c) Test T.6. Tests would be performed only on cells, because the voltage constraints imposed by the "Forced discharge" test procedure (see 38.3.4.6.3) precludes the test from being performed at the battery level. To stay within the prescribed "12 volts/V" constraint, the tests would be performed on series-connected strings composed of 3 or 4 cells, each having a nominal voltage in the range of 3 to 4 volts. Thus, for example, two 4-volt, or three 3-volt fully-charged cells would be connected with third 4-volt or fourth 3-volt test cell, that was at a 60% state-of-charge, and the specified load. This would force the test cell into an over-discharged state. The number of cells to be tested (10), is the same as that currently required by the Test Manual for "small" lithium cells. In addition, it is proposed that cells not be required to be subjected to this test when the voltage of the battery in which they are to be a component exceeds 12 volts, since, in such a case, the Test T.5 required to be performed on the battery evaluates essentially the same battery characteristics and is considered to be a more severe test.

(d) Charge state after cycling. For certain tests, the Test Manual requires that cells or batteries be cycled sufficiently "to reduce the capacity to 60%" before testing. For large lithium cells and batteries -specifically designed to maintain capacity through many recharge cycles -cycling through a sufficient number of cycles to reduce capacity to 60% of rated capacity could take many months -even years -and would be very expensive. Consequently, for practical reasons, it is proposed that large cells and batteries be cycled through a fixed minimum number of deep cycles (at least 50), and then tested in the state of charge (i.e., either fully charged or discharged) specified in the relevant test. These 50 or more deep cycles should be conducted between the fully charged and fully discharged states. This number of deep cycles is considered a sufficient number to reveal any of the cell or battery design problems or undesirable characteristics that the relevant tests are intended to identify.

10. Finally, the expert from the United States draws the Sub-Committee's attention to a deficiency with the Test T.4 (internal short circuit) test procedure that has come to light in attempting to apply the procedure to the testing of large batteries and cells. In this connection, it is noted that the 6mm diameter rod prescribed in the procedure as a means of effecting deformation of the cell or battery is of insufficient size to effect the degree of deformation of large cells or batteries necessary to create the required internal short circuit. If the Sub-Committee agrees, the expert from the United States will develop a proposal for consideration at the next session to address this deficiency with the basic Test T.4 test procedure.

Proposals

11. In light of the foregoing, the following amendments to the UN Recommendations are proposed:

(a) In Special Provision 230:

(i) Add a new first sentence to read:

"This entry applies to cells and batteries containing lithium in any form, including lithium polymer and lithium ion cells and batteries."

(ii) Add a note following ((a) to read:

"***Note:*** *For purposes of testing lithium cells and batteries, the Manual of Tests and Criteria draws a distinction between cells and batteries with aggregate lithium contents of not more than 12 g and 500 g, respectively, and cells and batteries with greater aggregate lithium contents.*"

(iii) Delete (b) and (c), and redesignate (d), (e), (f) and (g) as (b), (c), (d) and (e), respectively;

(iv) Revise new (d) [i.e., the current (f)] to read:

"each battery containing cells or series of cells connected in parallel is equipped with effective means of preventing dangerous reverse current flow (e.g., diodes, fuses, etc.);"

(b) In Special Provision 240, replace the words "or sodium batteries" after "powered by wet batteries" by the words "sodium batteries, or lithium batteries".

(c) Add a new Special Provision 28A to UN 3090 to read:

28A New, uncycled and uncharged lithium ion cells and batteries are not subject to these regulations if:

(a) The electrolyte does not meet the definition of any class or division in these regulations; or

(b) If the electrolyte meets the definition of a hazard class or division in these regulations, the electrolyte will not flow from a ruptured or cracked case and there is no free liquid to flow.

12. In addition, the following amendments are proposed to the Manual of Tests and Criteria:

(a) In 38.3.4.1 ("Test T.1") and in 38.3.4.2. ("Test T.2"):

1) Revise the introductory text in 38.3.4.1.2.2 and 38.3.4.2.2.2 to read:

"For cells in which the lithium content of the anode is not more than 12 g, and for batteries in which the aggregate lithium content of all cell anodes is not more than 500 g, the number and condition of cells and batteries to be tested are as follows:" [((a) to (f) unchanged]

2) Add a new 38.3.4.1.2.3 and 38.3.4.2.2.3 to read:

"For cells and batteries with lithium contents exceeding those specified in [38.3.4.1.2.2][38.3.4.2.2.2], the number and condition of cells and batteries to be tested are as follows:

(a) Only when cells are to be transported individually

(i) Ten cells which should be tested, at first cycle, in both fully charged and fully discharged states; and

(ii) Ten cells which should be tested after deep cycling a minimum of 50 times, in both fully charged and fully discharged states.

(b) Four batteries, which should be tested, at first cycle, in both fully charged and fully discharged states.

(c) Four batteries, which should be tested after deep cycling a minimum of 50 times, in both fully charged state and fully discharged states."

(b) In 38.3.4.3 ("Test T.3"):

1) Revise 38.3.4.3.2.2 to read:

"For cells in which the lithium content of the anode is not more than 12 g, and for batteries in which the aggregate lithium content of all cell anodes is not more than 500 g, the number and condition of cells and batteries to be tested are as follows:" [38.3.4.3.2.2.1 to 38.3.4.3.2.2.3 unchanged]

2) Add a new 38.3.4.3.2.3 to read:

"For cells and batteries with lithium contents exceeding those specified in 38.3.4.3.2.2, tests need not be performed on batteries, and the number and condition of cells to be tested are as follows:

(a) Ten cells which should be tested, at first cycle, in both fully charged and fully discharged states; and

(b) Ten cells which should be tested after deep cycling a minimum of 50 times, in both fully charged and fully discharged states."

(c) In 38.3.4.4 ("Test T.4"):

1) Transfer the first two sentences of 38.3.4.4.2.2 to the end of the "Introduction" section, (i.e., 38.3.4.4.1), and revise the third sentence to read:

"For cells in which the lithium content of the anode is not more than 12 g, the number and conditions of cells to be tested are as follows:" [((a) to (d) unchanged]

2) Add a new 38.3.4.4.2.3 to read (reminder of paragraphs to be renumbered):

"For cells with a lithium content exceeding that specified in 38.3.4.4.2.2, ten cells should be tested, at first cycle, in the fully charged state."

(d) In 38.3.4.5 ("Test T.5"):

1) Revise the introductory text in 38.3.4.5.2.2 to read:

"For cells in which the lithium content of the anode is not more than 12 g, and for batteries in which the aggregate lithium content of all cell anodes is not more than 500 g, the number and condition of cells and batteries to be tested are as follows:" [((a) and (b) unchanged]

2) Add a new 38.3.4.5.2.3 to read:

"For cells and batteries with lithium contents exceeding those specified in 38.3.4.5.2.2, batteries should be constructed with uncycled cells except for one in each series string which is deep cycled a minimum of 50 times. Four batteries are tested at first cycle in the fully charged state."

(e) In 38.3.4.6 ("Test T.6"):

(1) Revise 38.3.4.6.2.2 to read:

"For cells in which the lithium content of the anode is not more than 12 g, and for batteries in which the aggregate lithium content of all cell anodes is not more than 500 g, the number and condition of cells and batteries to be tested are as follows:" [38.3.4.6.2.2.1 to 38.3.4.6.2.2.3 unchanged]

2) Add a new 38.3.4.6.2.3 to read:

"For cells and batteries with lithium contents exceeding those specified in 38.3.4.6.2.2, tests need not be performed on batteries, and need only be performed on component cells when the battery voltage does not exceed 12 volts. When required to be tested, the number and condition of cells to be tested are as follows:

(a) Ten cells which should be tested, at first cycle, in the fully discharged state.

(b) Ten cells which should be tested, after deep cycling a minimum of 50 times, in the fully discharged state.

(f) In 38.3.4.7 ("Series T test criteria and method of assessing results"), 38.3.4.7.2 would be amended by replacing the words "subject to the mass requirements in Special Provision 230" with the words "not excepted from these Recommendations according to 38.3.4.7.1."